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Superheated steam pyrolysis of biomass elemental components and *Sugi* (Japanese cedar) for fuels and chemicals

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Abstract

To develop a novel noncatalytic biomass refinery process that can be used as a portable process, superheated steam pyrolysis was investigated to produce both carbonized solid fuels and chemicals using a large-scale reactor. Individual biomass components and native biomass (*Sugi*, Japanese cedar) were pyrolyzed. Between 150 and 400 °C, the vaporizing fractions of cellulose, xylan, and kraft lignin were summarized using a numerical model. Cellulose was converted to glycolaldehyde, furfural, 5-hydroxymethyl furfural and levoglucosan, whereas xylan was converted to glycolaldehyde, furfural, and acetic acid. Kraft lignin produced a slight yield of phenol and guaiacol. The total vaporization fraction of *Sugi* and its vaporizing rate were explained sufficiently using a numerical model based on the weighted average of the vaporizing properties of the individual components. However, the yields of phenol, guaiacol, and acetic acid were underestimated, while the yields of furfurals and levoglucosan were overestimated. Possible synergetic effects among chemicals in the superheated steam pyrolysis of native biomass were also discussed.

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Keywords: Biomass refinery; Superheated steam; Pyrolysis; Phenols; Numerical model

1. Introduction

Among renewable resources such as biomass, hydropower, solar, geothermal, wave, tidal, and wind resources, biomass is the only organic resource. Because of this, biomass is widely applicable causing interest to grow. Biomass utilization, especially unutilized agricultural and wood residues, could offer more environmentally acceptable processes, and could help conserve the limited supplies of fossil fuels (Horne and Williams, 1996a,b), which could lead to a sustainable global ecosystem. Biomass is particularly important as an energy and material source in developing countries. Mostly it is used in a primitive manner, such as direct combustion to obtain thermal energy. On the other hand, biomass can be converted to useful fuels and chemicals, such as those produced by oil refineries, to maintain our high degree of industrialization. In this sense, we should establish a "biomass refinery system" instead of today's "oil refinery system" for sustainable development.

Biomass processes are acceptable only when the products are more valuable than the feedstock. Because transportation energy cannot be ignored relative to the energy produced from collected biomass, refinery plant sites must be close to the biomass to minimize transportation energy. Moreover, biomass resources are dynamic and can change significantly over time (Noon and Daly, 1996). In this sense, we aim to develop an on-site mobile biomass conversion process that can be carried out on a truck. In this process, only the produced fuels and chemicals are transported from the biomass generating sites to the sites of consumption. This allows us to avoid

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energy-consuming biomass transportation. Furthermore, an efficient time schedule that coincides with the seasonal variation of biomass production reduces the process downtime.

Of the biomass conversion processes, interest in pyrolysis has been growing (Bridgwater and Kuester, 1998; Grassi et al., 1990). Pyrolysis is a thermochemical process that converts biomass into liquid, charcoal, and noncondensable gases by heating the biomass in the absence of air (Demirbaş, 2001a). Many biomass pyrolysis processes have been investigated (e.g., Caballero et al., 2000; Demirbaş, 2000, 2001a,b; Güllü and Demirbaş, 2001) among these, we focus on superheated steam pyrolysis.

Superheated steam has been utilized in drying processes since the turn of the century (Hager et al., 1997, 2000; Berghel and Renstrom, 2001; Schwartze and Bröcker, 2002). Using superheated steam in the drying process leads to substantial energy savings, if the vapor evaporating from the material is condensed and if condensation heat is recovered and used elsewhere in the process (Schwartze and Bröcker, 2002). Superheated steam has been used to treat biomass in liquefaction for fuel (White and Wolf, 1987), carbon activation for adsorbent materials (Vitidsant and Lortong, 1999), and torrefaction (Lipinsky et al., 2002a,b), which is a mild pyrolysis (200–280 °C) to improve the fuel properties of biomass (Pach et al., 2002). These techniques focus mainly on producing carbonized residue, or liquid fuel. However, we can obtain both carbonized residue and vaporized chemicals using superheated steam process in which the temperature is optimized to obtain both types of substance. Using carbonized residue to supply heat, this can be an energy self-sufficient process such as those used for pulp, paper, and forest products (Chum and Overend, 2001). These features of superheated steam pyrolysis apply to the on-site mobile process described above.

For this purpose, we investigated the vaporization characteristics during superheated steam pyrolysis especially as a function of temperature, which strongly affect biomass pyrolysis (Horne and Williams, 1996a,b). The objectives of this study were as follows: (1) To clarify the temperature dependency of superheated steam pyrolysis on elemental biomass components, i.e., cellulose, hemicellulose, and lignin. (2) To quantify the chemical materials vaporized from these components. (3) To discuss the applicability of the above clarified characteristics for native biomass using a numerical model.

To avoid the different thermal conditions between a small-scale experiment and actual large-scale equipment, we used a large-scale, superheated steam reactor that can mimic thermal conditions on a practical scale.

2. Experimental

2.1. Materials

Commercial microcrystalline cellulose (Avicel, Merck), xylan (from Birchwood, Sigma), and lignin (Alkali, Aldrich) were used as models of biomass structural components. *Sugi* (Japanese cedar, 2.5 × 2.5 × 2.5 cm cube, and sawdust particle diameter of 10–100 μm, inner part of the trunk, made in Japan), a popular building material in Japan, was used as native biomass. The shape and chemical composition of these samples are shown in Table 1. The carbon content was measured using the method described below. The cellulose, hemicellulose, and lignin contents were assayed according to a method described by Goering and Van Soest (1970).

2.2. Experimental apparatus

The superheated steam biomass pyrolysis reactor (Johnson Boiler Co. Ltd., Japan) used in this study is shown in Fig. 1. The reaction furnace contained three sections, each 15 L in volume and constructed of stainless steel. The furnace had a lid through which the sample could be inserted. Nine liters of ion-exchanged water was evaporated in each boiler per hour, and heated up to 700 °C in the superheater. The superheated steam was injected into the furnace. The temperature of these three sections was controlled independently using the steam temperature. The pyrolysis vapors leaving the furnace were passed through a stainless steel condenser. Condensable chemicals were obtained as a water solution. The solid residue was obtained after cooling down the furnace naturally to avoid self-ignition.

Table 1
Biomass samples used in the study

Sample	Cellulose (microcrystalline)	Hemicellulose (xylan, birchwood)	Lignin (kraft lignin)	*Sugi* (Japanese cedar)
Shape	Powder	Powder	Powder	2.5 × 2.5 × 2.5 cm/0.01–0.1 mm
C [%]	43.0	40.6	52.7	49.0
Cellulose [wt%]	–	–	–	49.7
Hemicellulose [wt%]	–	–	–	10.3
Lignin [wt%]	–	–	–	32.3
Apparent density [g/cm^3]	0.30	0.56	0.58	0.45

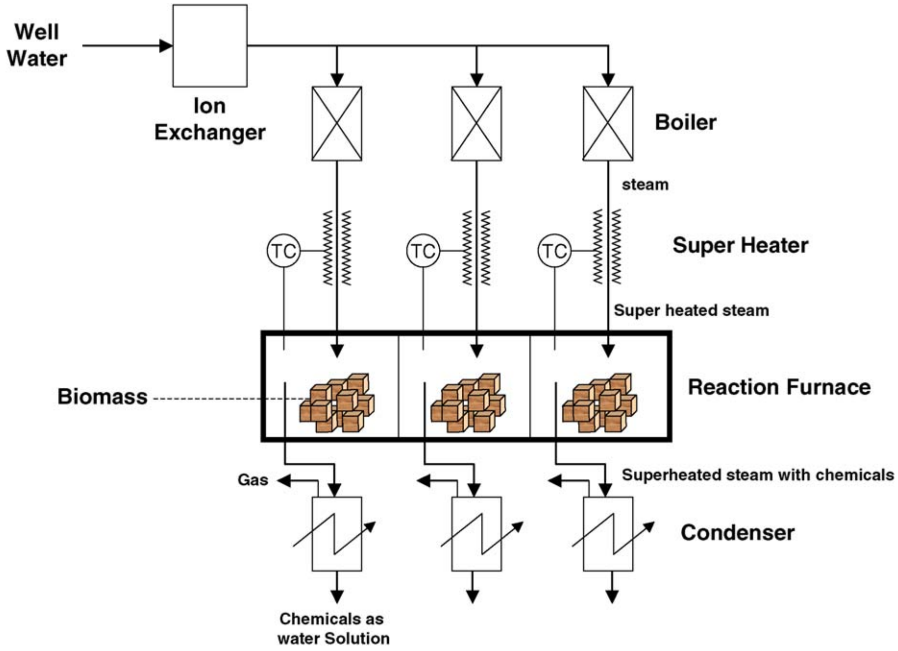

Fig. 1. Schematic diagram of superheated steam pyrolysis reactor used in this study.

2.3. Methods

Biomass samples were put into an aluminum foil tray of 10 × 20 cm in the bottom area and dried with an electrical oven (105 °C) for more than 12 h prior to the pyrolysis: cellulose (68–69 g dw = 29–30 g C), xylan (38–47 g dw = 16–19 g C), kraft lignin (46–47 g dw = 24–25 g C), and *Sugi* (block: 94–124 g dw = 46–61 g C; sawdust: 20–48 g dw = 10–23 g C).

The reaction furnace was heated with the superheated steam. When the temperature of each part reached the selected temperature (150–400 °C), the steam flow was temporarily stopped so the lid could be opened safely. The tray containing the biomass was carefully placed into the reaction furnace and the lid was closed immediately. Steam was then again introduced into the furnace to start the pyrolysis. The temperature profile since the introduction of superheated steam is shown in Fig. 2, indicating that the heating rate of this apparatus was 5–10 °C/min.

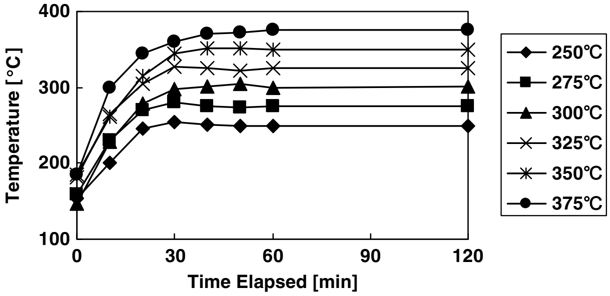

Fig. 2. Time course of the reactor temperature after introducing superheated steam.

The low molecular weight chemicals were vaporized in the furnace and moved to the condenser by the superheated steam. The steam containing the chemicals was cooled and condensed in a condenser with tap water (ca. 10–15 °C) leaving the noncondensable chemicals such as CO, CO_2, and CH_4 as effluent gas. In some cases, the effluent noncondensable gas was collected and its amount and composition were measured. The condensed steam (called "eluent liquid" below) was sampled at the condenser every 5–30 min for 120 min after starting the pyrolysis. The weight of condensed water was also measured. The steam flow was then stopped and the furnace was cooled naturally. The recovered solid residue was dried in an electrical oven (105 °C) for more than 12 h, and weighed.

The dissolved organic carbon (DOC) concentration of the eluent liquid and elemental carbon contents of the solid residue were measured with using a TOC analyzer (Shimadzu, Japan) model TOC-500, and a CHN analyzer (Perkin–Elmer, USA) model 2400-II, respectively. Quantitative analyses of phenolic compounds, furanic compounds, anhydrosugars, carboxylic acids, and aldehydes in the eluent liquids were performed using an HPLC system (LC-10 series, Shimadzu, Japan) or an GC system (GC-17 series, Shimadzu, Japan). The conditions of the analysis are as follows:

(1) Phenols (for kraft lignin)
Column: Shodex Inertsil ODS-3 (Showa Denko, Japan) 4.6 mm i.d. × 250 mm length, 30 °C.
Mobile phase: CH_3OH/0.01 M H_3PO_4 in H_2O = 3/7, 1.0 mL/min.

Detect: UV 254 nm absorbance, SPD-10A (Shimadzu, Japan).
Injection volume = 20 μL.
Retention time (min): 5-HMF = 5.0; resorcinol = 6.8; maltol = 7.0; furfural = 7.6; cathecol = 9.2; *p*-hydroxybenzoic acid (Internal Standard) = 12.1; vanilin = 16.0; syringaldehyde = 17.2; phenol = 17.7; guaiacol = 21.9; syringol = 25.1.

(2) Phenols (for *Sugi*)
System: Shimadzu GC 17 system.
Column: DB-1 (J&W Scientific, USA), thermal gradient (50–300 °C).
Carrier: He, 1.0 mL/min.
Detect: FID.
Injection volume = 0.5 μL.
Retention time (min): phenol = 10.8; guaiacol = 14.3; cathecol = 17.7; methylguaiacol = 17.7; resorcinol = 20.1; ethylguaiacol = 20.5.

(3) Levoglucosan
Column: Shodex Asahipak NH_2P-50 (Showa Denko, Japan) 4.6 mm i.d. × 250 mm length, 30 °C.
Mobile phase: 75% CH_3CN in H_2O, 1.0 mL/min.
Detect: Refractive Index Detector RID-10A (Shimadzu, Japan).
Injection volume = 20 μL.
Retention time (min): levoglucosan = 4.5.

(4) Carboxylic acids, aldehydes, and furanic compounds
Column: Shodex SH1011 (Showa Denko, Japan) 8.0 mm i.d. × 300 mm length, 50 °C.
Mobile phase: 0.01 N H_2SO_4 in H_2O, 1.0 mL/min.
Detect: Refractive Index Detector RID-10A (Shimadzu, Japan).
Injection volume = 20 μL.
Retention time (min): glucuronic acid = 6.6; malonic acid = 7.7; glycelaldehyde = 8.8; succinic acid = 9.1; pyruvaldehyde = 9.2; glycolaldehyde = 9.4; levoglucosan = 9.4; dihydroxyacetone = 10.0; formic acid = 10.2; acetic acid = 11.2; adipic acid = 11.7; levulinic acid = 12.0; propionic acid = 12.9; acetaldehyde = 13.2; *n*-butyric acid = 15.7; 5-HMF = 22.0; furfural = 33.2.

Calorific values of *Sugi* and its solid residue were measured using a calorific meter (Ogawa sampling, Japan) model OSK-200.

3. Results and discussion

3.1. Vaporizable fraction of biomass components

The carbon balances of cellulose, xylan, and kraft lignin after superheated steam pyrolysis were determined at various temperatures. The fraction of eluted and residual carbon after a 120 min treatment of each biomass component as a function of temperature is shown in Fig. 3. The vaporization was completed by 120 min as judged by the variation of carbon concentration in the eluent liquid. In all cases, the vaporized fraction increased with increasing temperature, whereas the

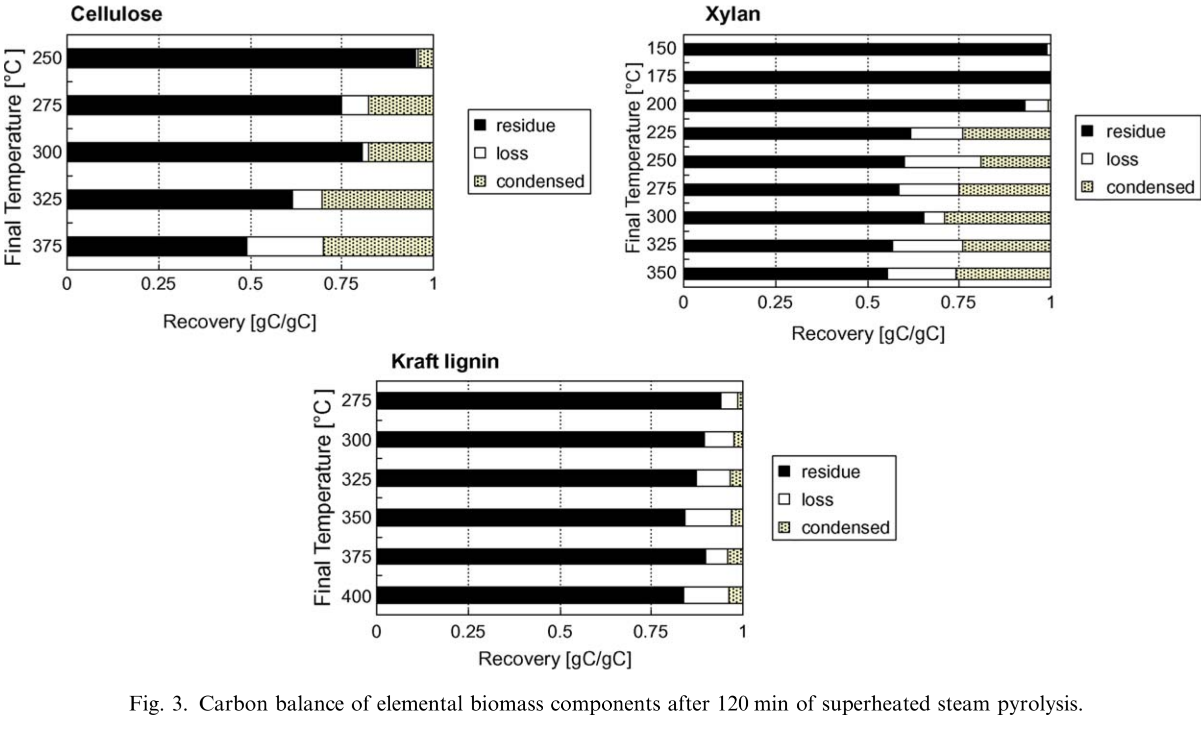

Fig. 3. Carbon balance of elemental biomass components after 120 min of superheated steam pyrolysis.

temperature dependence of vaporizing fraction differed between components. Only a small amount of cellulose (5%) could be vaporized at a low temperature (250 °C), whereas about half was vaporized at a high temperature (375 °C). A small fraction of xylan was vaporized at temperatures lower than 175 °C, whereas the vaporized fraction suddenly increased within a temperature range between 200 and 225 °C, and did not significantly vary over 225 °C. The temperature dependency of kraft lignin vaporization was similar to that of cellulose; however, the vaporized fraction was relatively small. The recovery loss also increased with temperature. This loss is possibly due to the production of noncondensable gases and tarry matters adhered to the wall of the reactor. The noncondensable gas production from cellulose was measured in another experiment. The production ratios based on carbon were as follows:

250 °C: CO (0.5%), CO_2 (0.7%), CH_4 (not detected);
300 °C: CO (0.4%), CO_2 (0.8%), CH_4 (not detected);
350 °C: CO (1.7%), CO_2 (4.2%), CH_4 (0.03%).

The amounts of noncondensable gas were relatively low, and the loss was therefore mainly due to the tarry matters.

The temperature dependence of pyrolysis can be described quantitatively using a numerical model. Many models have been used to describe the pyrolysis of cellulose (Bilbao et al., 1987a,b, 1989; Antal Jr. and Várhegyi, 1995; Várhegyi et al., 1997), xylan (Bilbao et al., 1989; Di Blasi and Lanzetta, 1997), and kraft lignin (Bilbao et al., 1989; Caballero et al., 1995). We employed a simple numerical model proposed by Caballero et al. (1995) to describe the pyrolytic properties of biomass. In this model, biomass is assumed to consist of many “fractions”. A given fraction starts to decompose only if the biomass temperature is greater than or equal to a characteristic temperature T_R of this fraction. A distribution function of T_R that describes the fraction of biomass that can begin to decompose at a given temperature is defined with a function named C. Consequently,

$$\int_0^\infty C\,\mathrm{d}T_R = 1. \tag{1}$$

In the most simple schemes, biomass decomposition can be expressed by the reaction

$$B \to sS + vV, \tag{2}$$

where B is the biomass, V is the vaporized fraction, S is the solid residue, and s and v are the yield coefficients expressed as the “weight of solids or volatile products formed/weight of biomass decomposed”. The biomass decomposition is described as

$$\frac{\mathrm{d}w}{\mathrm{d}t} = -k_0 \exp(-E/RT)(w - w_\infty), \tag{3}$$

where w is the biomass fraction [−], t is the time [s], k_0 is the frequency factor [s^{-1}], E is the activation energy [J mol^{-1}], R is the gas constant [J mol^{-1} K^{-1}], T is the temperature [K], and w_∞ is the residue fraction at time infinity [−]. w_∞ can be written as

$$w_\infty(T) = \int_0^T sC\,\mathrm{d}T_R + \int_T^\infty C\,\mathrm{d}T_R \tag{4}$$

Assuming that s does not change with temperature and assuming a Gaussian distribution for C, the C curve and w_∞ can be described as shown in Fig. 4.

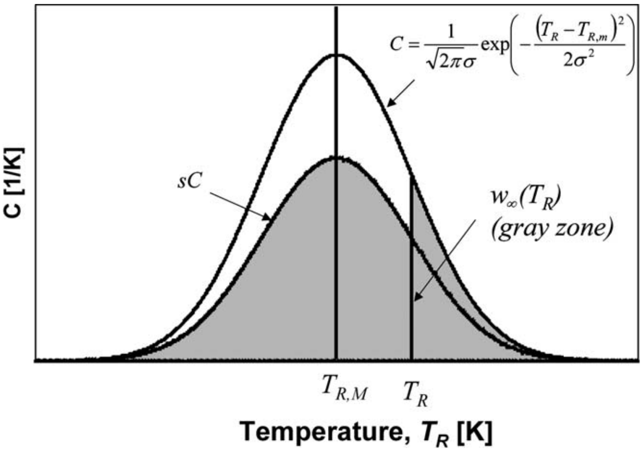
$C = \frac{1}{\sqrt{2\pi}\sigma}\exp\left(-\frac{(T_R - T_{R,m})^2}{2\sigma^2}\right)$
sC
$w_\infty(T_R)$
(gray zone)
C [1/K]
$T_{R,M}$
T_R
Temperature, T_R [K]

Fig. 4. C curve assumed in this study.

When the vaporizing reaction with superheated steam occurred under a certain temperature T_i, Eq. (2) can be rewritten as

$$w_\infty(T_i) = s\int_0^{T_i} C\,\mathrm{d}T_R. \tag{5}$$

We assumed that the vaporizing fractions of cellulose, xylan, and kraft lignin do not change over 375 °C, 350 °C, and 400 °C, respectively, based on our observations. Thus, s values are estimated as 0.5, 0.55, and 0.85 for cellulose, xylan, and kraft lignin, respectively. Using these s values, $T_{R,M}$ and σ were estimated with the least-square method based on the residual carbon fraction after a 120 min treatment. In this estimation, the parameter fluctuating ranges were as follows: in the case of cellulose, $T_{R,M}$ was fluctuated between 250 and 350 °C with 5 °C interval, and σ was fluctuated between 20 and 70 °C with 5 °C interval. In the case of xylan, $T_{R,M}$ was fluctuated between 200 and 250 °C with 5 °C interval, and σ was fluctuated between 5 and 30 °C with 5 °C interval. In the case of kraft lignin, $T_{R,M}$ was fluctuated between 250 and 350 °C with 5 °C interval, and σ was fluctuated between 10 and 60 °C with 5 °C interval. The comparison between observation and calculation with the finally estimated $T_{R,M}$ and σ for cellulose, xylan, and kraft lignin are shown in Fig. 5a–c, respectively. Consequentially, cellulose, xylan, and kraft lignin were vaporized between 250 and 340 °C, 200 and

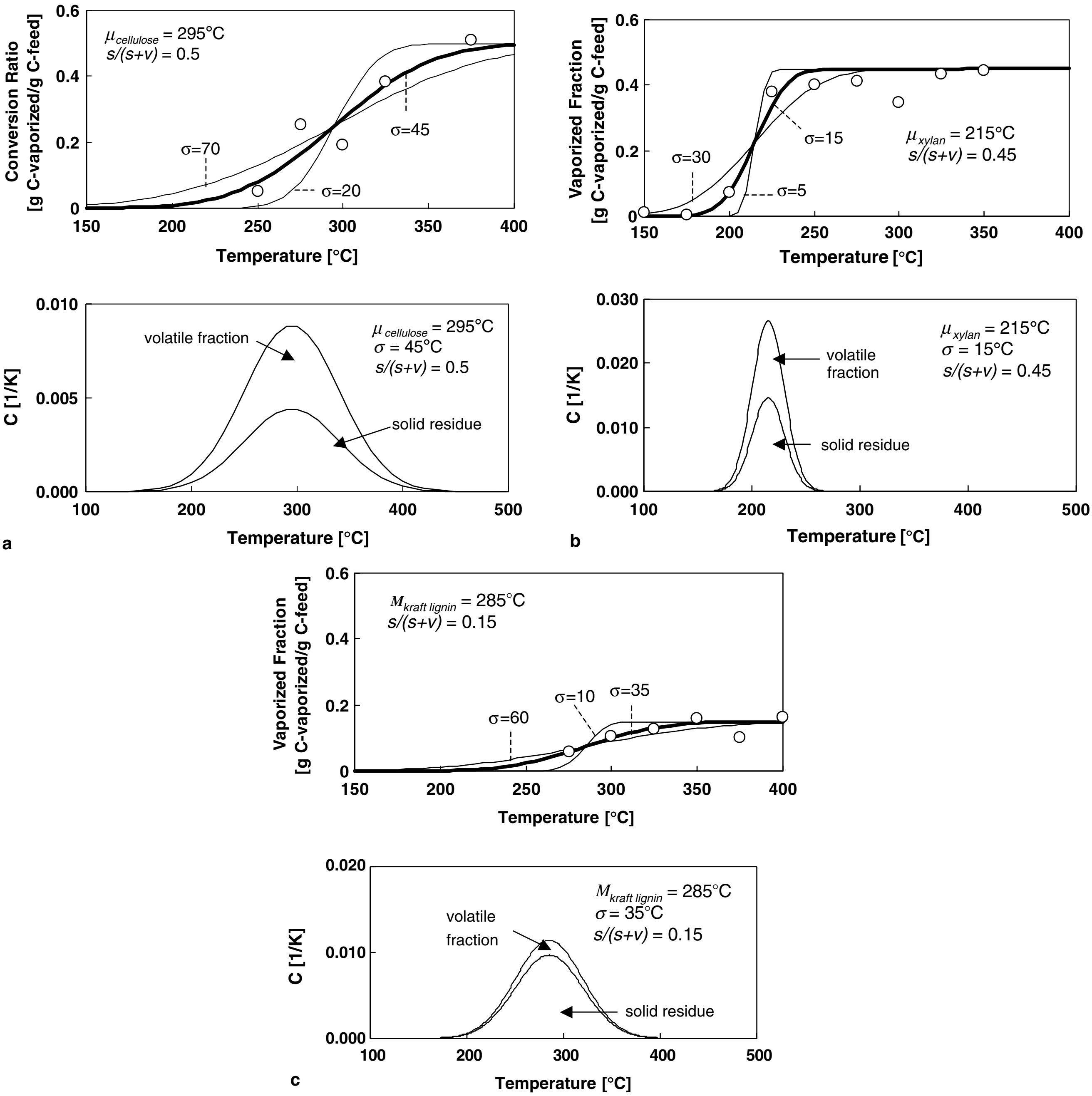

Fig. 5. Estimations of σ and μ based on observations (upper graph) and resultant C curve for (a) cellulose pyrolysis (lower graph), (b) xylan pyrolysis (lower graph), (c) kraft lignin pyrolysis (lower graph).

230 °C, and 250 and 320 °C, respectively. And the temperature sensitivity in terms of the standard deviation of the C curve was 2–3 times as high as that of cellulose and kraft lignin.

In the torrefaction process, biomass is treated at 200–270 °C to vaporize the hemicellulose fraction. The pyrolysis property of xylan is compatible with this operational condition, meaning that hemicellulose pyrolysis using superheated steam is similar to the pyrolysis that occurs in torrefaction. Torrefaction produces a good solid fuel with a stable moisture content of about 3%, mass reduction by 20–30%, retention of 80–90% of its original energy content, and the removal of smoke-producing agents (Lipinsky et al., 2002a,b). These purposes can be fully achieved by pyrolyzing hemicellulose (=xylan) with superheated steam between 200 and 240 °C. In contrast, to obtain vaporized chemicals, we should operate the superheated steam at 250–340 °C in order to vaporize cellulose and lignin which are the main part of biomass (e.g., 80% of *Sugi*, see Table 1).

3.2. Vaporization rate of biomass components

The previous section discussed the potential of superheated steam pyrolysis of biomass components. In this section, the rate of the vaporization process is described. The pyrolysis rate was estimated indirectly using the time variation of the organic carbon concentration of the eluent liquid. The rate process was described using Eq. (3), where $T_{\mathrm{R,M}}$ and σ were estimated in a previous section. Parameters k_0 and E can be estimated from experimental observations. Note that the time variation of the total vaporized fraction was not measured directly due to the recovery loss of tar and noncondensable gases mentioned above. Thus, we use the following equation to estimate the total vaporizing fraction:

$$C_{\mathrm{vaporized,total}} = s \cdot C_{\mathrm{eluted,total}} \tag{6}$$

where $C_{\mathrm{vaporized,\,total}}$ is the total vaporized carbon at time t, and $C_{\mathrm{eluted,\,total}}$ is the accumulation of eluted carbon at time t. The temperature is varied with time as in Fig. 2, meaning that it is difficult to obtain an exact solution to Eq. (3). Thus, by solving Eq. (3) numerically, parameters k_0 and E were determined by referring the least-square between calculations and observations. Each parameter was fluctuated in the range depicted in Fig. 6a–c. And the fluctuated interval were 25 s^{-1} and 1 kJ mol^{-1} for k_0 and E, respectively. We employed STELLA Research J 5.1.1 for Windows (High Performance Systems Inc.) to obtain the numerical solution.

The estimation of parameter k_0 and E for cellulose, xylan, and kraft lignin are shown in Fig. 6a–c, respectively. As a result, sufficient parameter values to describe the pyrolysis properties of each component were obtained.

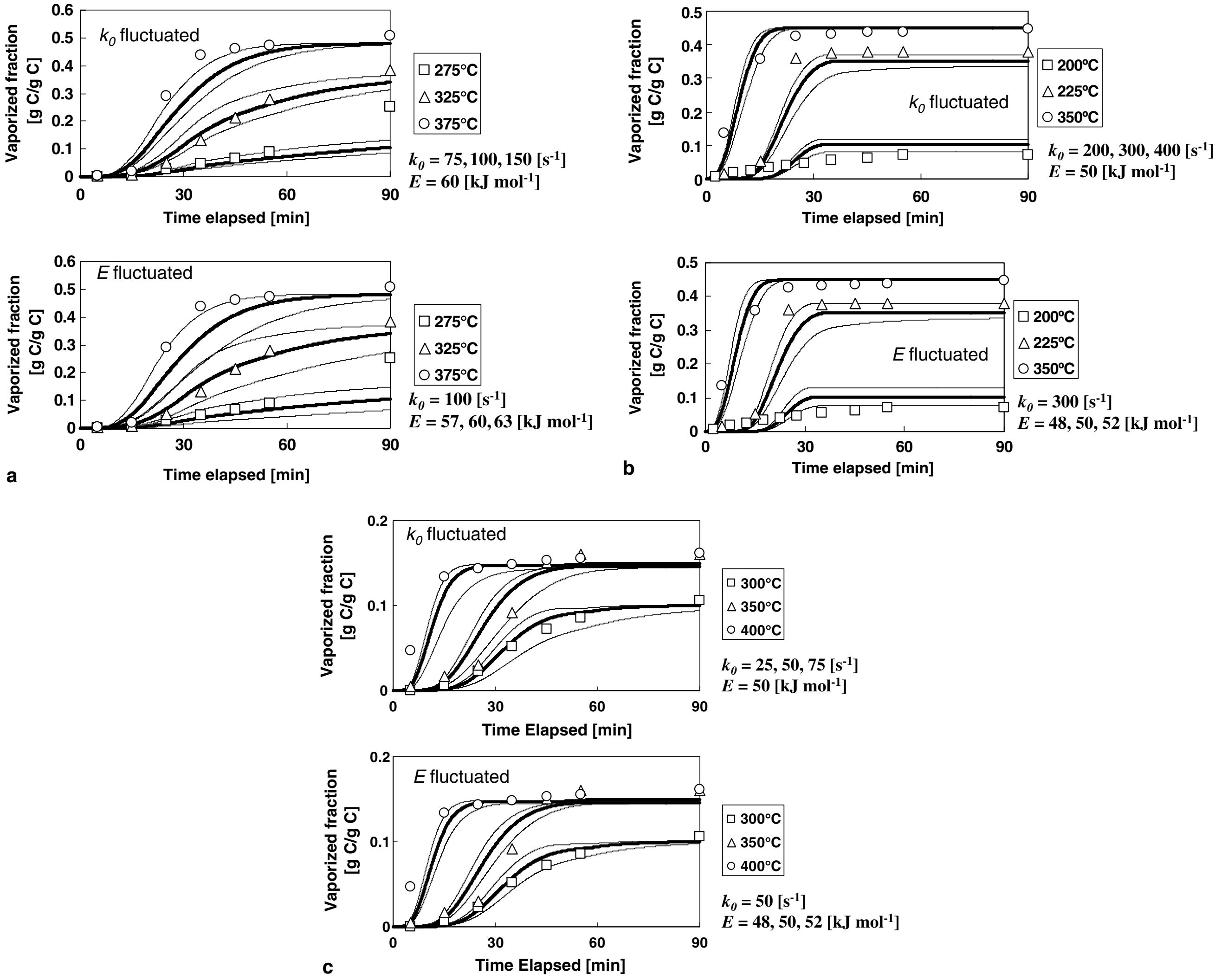

Fig. 6. Estimations of k_0 (upper graph) and E (lower graph) for (a) cellulose pyrolysis and vaporization, (b) xylan pyrolysis and vaporization, (c) kraft lignin pyrolysis and vaporization. (Thick lines: calculation using median of fluctuated parameter; thin lines: calculation using maximum and minimum of fluctuated parameter.)

3.3. Vaporization fractions of *Sugi*

As mentioned in Section 2.3, superheated steam pyrolysis using *Sugi* as an example of native biomass was performed. The carbon balance of superheated steam pyrolysis of *Sugi* is depicted in Fig. 7. Three experimental cases, namely, the *Sugi* block case without measuring noncondensable gas, the *Sugi* block case with measuring noncondensable gas, and the *Sugi* sawdust case without measuring noncondensable gas, are shown. There was no obvious difference between block and sawdust pyrolysis, indicating that the size of biomass within the range of millimeter to centimeter might not affect the pyrolysis of *Sugi*. The noncondensable gas (composition: $CO = 44$–55%; $CO_2 = 44$–53%; $CH_4 = 1$–4%) was produced at about 3–4% of feed carbon between 250 and 350 °C. The recovery loss was increased with the pyrolysis temperature. Note that in the case of 350 °C pyrolysis, the produced noncondensable gas accounted for only 15% of the recovery loss. Therefore, the recovery loss mainly consisted of the tarry compounds that adhere to the walls of the reactor, pipeline, and condenser, especially in the high temperature (325–375 °C) pyrolysis.

The predictability of the above-mentioned pyrolysis models of the components was also confirmed in this experiment. Assuming that *Sugi* consists of only cellulose, hemicellulose, and lignin, the residue fraction of *Sugi*($w_{\infty,Sugi}$) at infinite time can be calculated using the following equation:

$$w_{\infty,Sugi}(T) = f_{\text{cellulose}} \cdot w_{\infty,\text{cellulose}}(T) + f_{\text{hemicellulose}} \cdot w_{\infty,\text{hemicellulose}}(T) + f_{\text{lignin}} \cdot w_{\infty,\text{lignin}}(T), \tag{7}$$

where $f_{\text{cellulose}}, f_{\text{hemicellulose}}$, and f_{lignin} are the fractions of cellulose, hemicellulose, and lignin of *Sugi*, respectively, and $w_{\infty,\text{cellulose}}$, $w_{\infty,\text{hemicellulose}}$, and $w_{\infty,\text{lignin}}$ are the residue fraction of cellulose, hemicellulose, and lignin, respectively, at time infinity. Furthermore, assuming that the reaction of *Sugi* pyrolysis using superheated steam is complete at 120 min, and the residue fraction of hemicellulose and lignin are equal to that of xylan and kraft lignin, respectively, we get the following equation:

$$w_{120\,\text{min},Sugi}(T) = f_{\text{cellulose}} \cdot w_{\infty,\text{cellulose}}(T) + f_{\text{xylan}} \cdot w_{\infty,\text{xylan}}(T) + f_{\text{kraft lignin}} \cdot w_{\infty,\text{kraft lignin}}(T) \tag{8}$$

$w_{\infty,\text{cellulose}}(T)$, $w_{\infty,\text{xylan}}(T)$, and $w_{\infty,\text{kraft lignin}}(T)$ are already described as Eq. (5) and Fig. 5. As in Eq. (8), the time course of the residual fraction can be predicted as

$$w_{t,Sugi}(T) = f_{\text{cellulose}} \cdot w_{t,\text{cellulose}}(T) + f_{\text{xylan}} \cdot w_{t,\text{xylan}}(T) + f_{\text{kraft lignin}} \cdot w_{t,\text{kraft lignin}}(T). \tag{9}$$

Furthermore, to estimate the predictability of the models, the model prediction error ($\varepsilon_{\text{pred}}, \%$) is calculated using the following equation:

$$\varepsilon_{\text{pred}} = \frac{(w_{\text{obs}} - w_{\text{calc}})}{w_{\text{calc}}} \cdot 100 \tag{10}$$

where, w_{obs} and w_{calc} are the observed and calculated residue fractions, respectively.

The observations and calculation of the vaporized fraction (i.e., $1 - w_{120\,\text{min},\,Sugi}$) of *Sugi* after 120 min pyrolysis by superheated steam as a function of temperature

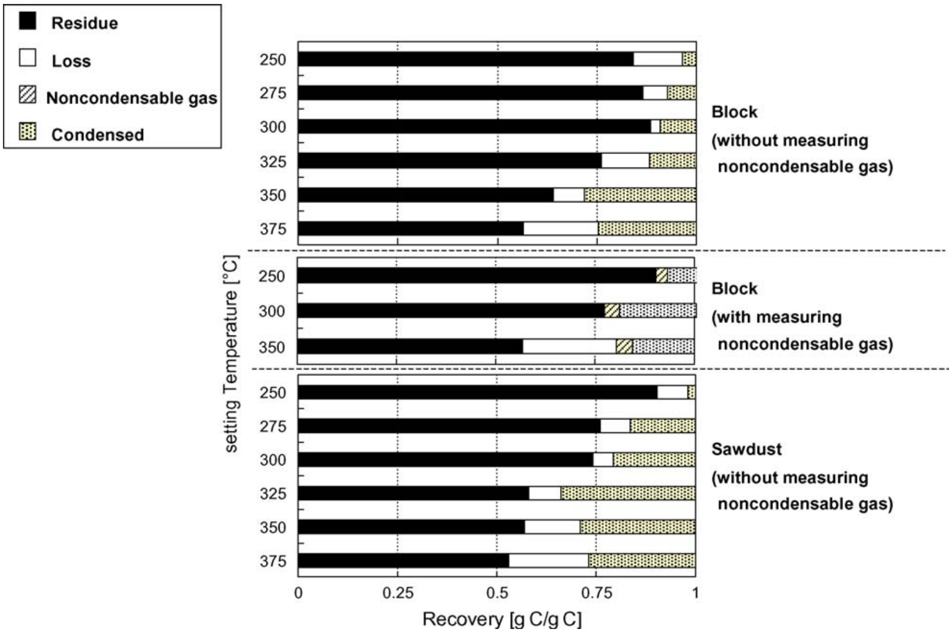

Fig. 7. Carbon balance of *Sugi* after 120 min of superheated steam pyrolysis.

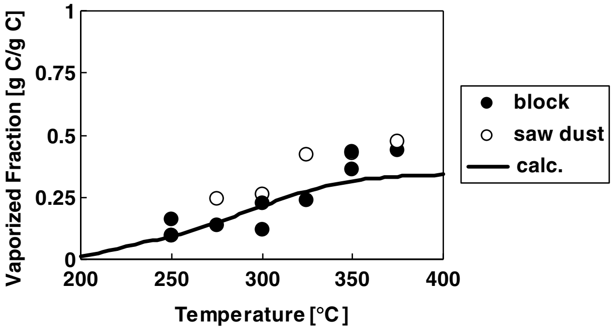

Fig. 8. Vaporized fraction of *Sugi* after 120 min of superheated steam pyrolysis as a function of temperature.

is shown in Fig. 8. The vaporization obviously depends on temperatures from 250 °C to 375 °C. The model predict this tendency (the model prediction error calculated by Eq. (10) was within the range of −5 to +21%), meaning that the vaporization of *Sugi* can be described as a combination of the pyrolysis properties of cellulose, xylan, and kraft lignin. In the same manner, the time course of the vaporization of *Sugi* was also predicted for the 350 °C case. Satisfactory agreement between the observations and calculations (the model prediction error calculated by Eq. (10) was within the range of −9 to +6%) is shown in Fig. 9. This idea that the pyrolytic properties of lignocellulose can be regarded as a weighted average of the pyrolytic properties of individual constituents is widely used in the literature (Bilbao et al., 1989). Such an attempt using "Pinaster" pine wood was demonstrated in Bilbao et al. (1989), and close agreement was obtained between observation and prediction. In this study, the pyrolysis of wood with known composition using superheated steam was also predicted using the weighted average of the pyrolytic properties of individual constituents. This information is useful for designing the operating conditions for superheated steam pyrolysis of various woods.

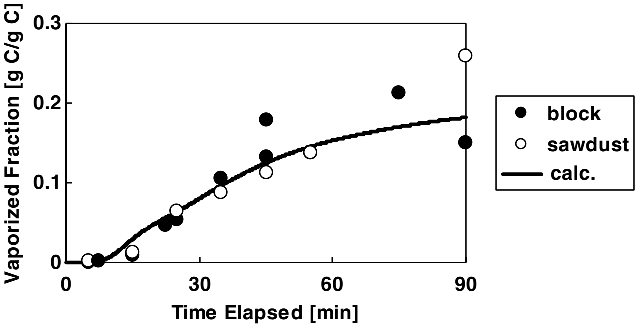

Fig. 9. Time course of vaporized fraction of *Sugi* under superheated steam pyrolysis (300 °C).

The carbon content and the calorific value of solid residue are tabulated in Table 2. Energy preservation, calculated based on the yield of solid residues, is also shown in this table. Calorific preservation decreased abruptly at temperatures of more than 325 °C. However, energy conservation at 375 °C (52%) exceeded that of conventional charcoal making (20%) and was comparable to commercial carbonization processes (up to 55%). Thus, superheated steam pyrolysis from 250 to 375 °C is useful for producing charcoal fuel.

3.4. Chemicals quantified in the eluent liquids

As mentioned in Section 1, the primary target of our biomass refinery system is to produce not only fuels, but also chemicals such as plastic-derivable monomers. The contents of each eluent liquid analyzed using HPLC is shown in Fig. 10. Regarding lignin, slight amounts of phenol and guaiacol were found (data not shown). Glycolaldehyde, levoglucosan, 5-HMF, and furfural are the main products produced from cellulose. Under 325 °C, the recovery of these main products increased with temperature, whereas little variation was observed at >325 °C. Small amounts of levulinic acid, glyceraldehyde, propionic acid, and valeic acid were also detected in the eluent liquid of cellulose. Levoglucosan is the precursor of various functional polymers (e.g., Hatanaka et al., 1998; Lazdina and Apsite, 1999). Miura et al. (2001) showed high yields of levoglucosan from cellulose-rich materials (12% from filter paper, 6% from used paper, and 2.6% from larch log, dry basis) through the use of a microwave reactor. The levoglucosan yields using superheated steam is about 2% in carbon basis at 350–375 °C. A comparison with the levoglucosan yield of filter paper via microwave pyrolysis (12%)

Table 2
Carbon contents and calorific value of *Sugi* before and after super heated steam treatment

	Carbon contents (%)	Calorific value (MJ/kg dw)	Calorific value (MJ/kg C-residue)	Solid carbon yield (g C-residue/g C-biomass)	Energy preservation (MJ-residue/MJ-biomass)
Nontreated	48.9	21.3	43.6	–	–
250 °C treatment	52.9	23.7	44.8	0.84	0.86
275 °C treatment	56.7	24.5	43.3	0.87	0.86
300 °C treatment	60.0	27.0	45.0	0.88	0.91
325 °C treatment	71.8	28.4	39.6	0.76	0.69
350 °C treatment	73.8	27.3	37.0	0.64	0.54
375 °C treatment	73.9	29.6	40.0	0.56	0.52

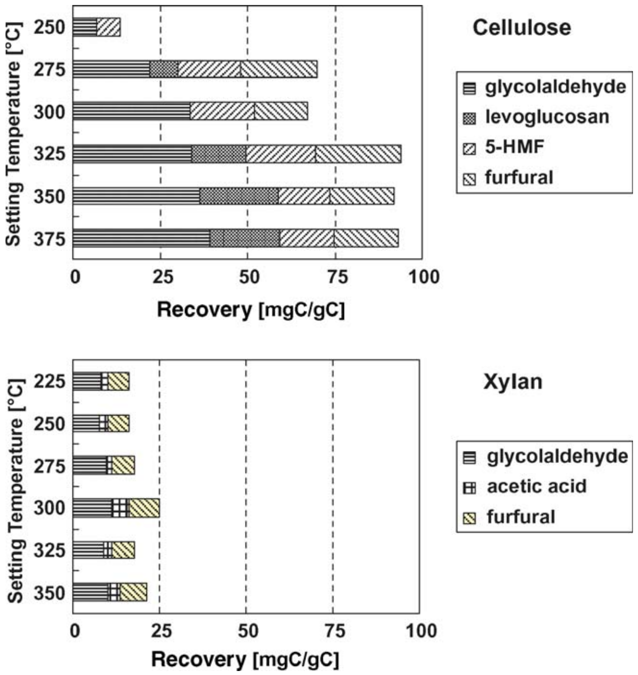

Fig. 10. Chemicals observed in the eluent liquids of cellulose and xylan treatments.

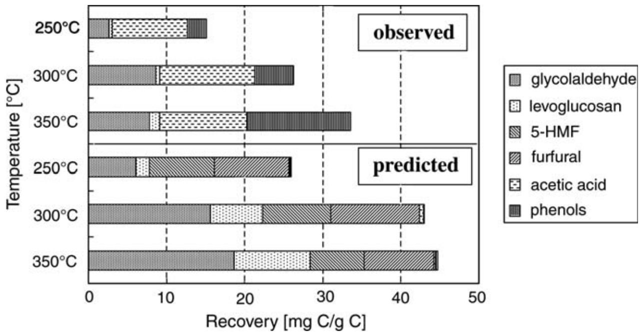

Fig. 11. Products from superheated steam pyrolysis of *Sugi* (350 °C) and its comparison with the prediction based on its elemental components. (phenols = phenol + guaiacol).

revealed that the efficiency of the superheated steam pyrolysis is about 1/6 of that of microwave pyrolysis. However, considering its simplicity, the superheated steam pyrolysis of cellulose-rich biomass is a promising method for obtaining levoglucosan, especially when applied to an on-site mobile process. Glycolaldehyde had been identified as a major component of the oxygenated products born of cellulose pyrolysis (Byrne et al., 1966). Two major pathways are recognized during cellulose pyrolysis: one leads to the formation of levoglucosan as a relatively stable product and the second yields glycolaldehyde (Antal Jr. and Várhegyi, 1995). These pathways can be selected using certain treatments. Especially, ash removal increases the levoglucosan yield (Piskorz et al., 1989). Polymer synthesis from 5-HMF and furfural is also possible (Gandini and Belgacem, 1997; Kunz, 1993). From these considerations, we can recover the precursor of polymers from cellulose as ca. 9% in carbon basis (5.9% as levoglucosan and glycolaldehyde; 1.5% as 5-HMF; and 1.9% as furfural). On the other hand, glycolaldehyde, furfural, and acetic acid were eluted from xylan. However, their total conversion ratios were very low (about 1% in carbon basis).

The chemical composition of *Sugi*-derived eluent liquid is shown in Fig. 11. The main products from *Sugi* were levoglucosan, glycolaldehyde, acetic acid, phenol, and guaiacol. Small amounts of levulinic acid, propionic acid, valeic acid, and resorcinol were also detected. Phenol and guaiacol can be used as the precursor of phenol resin, which is one of the oldest artificial plastics. Acetic acid can be used to produce cellulose acetate, which is valued as a biodegradable plastic. Phenol and guaiacol are derived from lignin. The yield of phenol and guaiacol is 1.6 wt% (dry basis), and about 5 wt% (total lignin basis). Phenols are contained in the tar produced by biomass pyrolysis (e.g., Brage et al., 1997; Morf et al., 2002). Limited information is available in the literature concerning the production of phenols from biomass feedstocks, largely because the products are complex and separation is costly (Amen-Chen et al., 2001). Samolada et al. (1992) and Samolada and Vasalos (1994) showed high phenol yield as 12 wt% dry basis from Greek fir wood in a fluidized bed reactor at 520 °C, and concluded that temperature significantly affects the yield of phenolic compounds as follows:

$$Y_{\text{liquid}}(\text{wt\%}) = 11.54 - 1.3X - 7.17X^2, \tag{11}$$

$$X = (T - 560)/160, \tag{12}$$

where X is the dimensionless pyrolysis temperature, and T is the pyrolysis temperature [°C]. According to these equations, a yield of 3.45% is calculated at 375 °C. In contrast, our resultant phenol yield (1.1 wt%) was about half of this. The difference was due to differences regarding the method of operation used, especially regarding heating rate (Samolada's process was a fast pyrolysis process. The heating rate was estimated as 1000 °C/s, which is about 10,000 times larger than our process.) and sample size (360–800 μm in Samolada's work; 2.5 × 2.5 × 2.5 cm in this work), which affects tar production. However, we measured phenolic compounds only in the eluent liquid. Many phenolic compounds in tar could not be recovered in this experiment. Therefore, the gross conversion to phenols would increase with the application of an effective tar treatment. The development of effective tar-treatment technologies (e.g., Horne and Williams, 1996a,b; Morf et al., 2002) and separation (e.g., Brage et al., 1997) are required to make superheated steam processes more suitable as a biomass refinery.

Furthermore, compared to the chemicals from each biomass component, a simple linear prediction is also shown in Fig. 11. The prediction was performed using the chemical stoichiometric relations of cellulose, hemicellulose, and lignin of *Sugi* as follows:

$$p_{Sugi,i} = x_{Sugi,j} \cdot \sum_{j} p_{j,i}, \quad j = \text{cellulose, hemicellulose, lignin} \tag{13}$$

where $p_{Sugi,i}$ is the production of i from *Sugi*, $x_{Sugi,j}$ is the j's fraction in *Sugi*, and $p_{j,i}$ is the production of i from j.

There was an obvious difference between the observed and the predicted chemicals in the eluted water solution. The productions of 5-HMF, furfural, and levoglucosan were lower than predicted. We consider that one reason for the decrease in the yields of furfurals was the formation of phenol resin between furfurals and phenols (Brown, 1952), caused by the coexistence of monomeric phenols. Further, we thought that the yield of levoglucosan as a water solution was decreased due to its dissolving in the tarry matters, of which there was a relatively large amount in the *Sugi* case (the "loss" in Fig. 7) compared to that in the cellulose case (the "loss" in Fig. 3). This consideration was based on the fact that the levoglucosan has been obtained as tarry matters in previously reported cellulose pyrolysis (Miura et al., 1983, 2000).

An unexpected yield of phenols was obtained. Compared with the yield from kraft lignin, it was remarkable. The lignin pyrolysis products were strongly affected by additives (Amen-Chen et al., 2001). For example, the coexistence of a hydrogen donor such as tetralin (1,2,3,4-tetrahydronaphthalene) or phenol gave a higher yield of monomeric phenols from lignin due to its hydrogen donation activity for phenoxy radicals, which appeared after lignin ether bond cleavage (Connors et al., 1980; Davoudzadeh et al., 1985). Further, McMillen et al. (1987) showed that hydrogen donor solvents could also be free radical promoters, and Omori et al. (1998) indicated that holocellulose acts as a hydrogen donor, reducing the radical species before the occurrence of radical recombination when lignin is pyrolyzed. Therefore, we concluded that the coexisting holocellulose in *Sugi*, which does not exist in kraft lignin, acts as hydrogen donor, and as a result, the decomposition and vaporization rate are accelerated in actual *Sugi* pyrolysis compared with the calculation based on pyrolysis of each of the elemental compounds. The increase in the yield of monomeric phenols was evidence of this speculation.

However, the yield of acetic acid was also increased. In biomass pyrolysis at a relative low temperature, the acetic acid was produced from an acetyl group in hemicellulose. However, based on the observation in the *Sugi* pyrolysis, the yield of acetic acid was far higher than the amount of the acetyl group in hemicellulose contained in *Sugi*. The mechanism was not clear due to limited information, though the interactions of biomass elemental compounds and their derivatives during superheated steam pyrolysis resulted in an increase in acetic acid.

4. Conclusion

Superheated steam has been utilized as a drying technology and carbonization technology. In this study, we focused on its possible use as a mobile biomass refinery process that produces not only carbonized fuel but also chemical feedstock, especially for polymers. In conclusion, the following points are summarized:

1. The vaporized fractions of cellulose, xylan (as hemicellulose), and kraft lignin (as lignin) using superheated steam as a function of temperature were summarized using a numerical model.
2. Furfural and glycolaldehyde were the main products as polymer precursors from cellulose and xylan. 5-hydroxymethyl furfural and levoglucosan were also produced from cellulose.
3. The overall vaporization fractions of *Sugi* (Japanese cedar) could be described in terms of the fractions of cellulose, xylan, and lignin. However, the productions of phenol and guaiacol surpassed the predicted amounts. This indicates significant synergic effects of the production of phenol compounds from native biomass lignin.

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